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(54) METHOD FOR DIRECTLY FORMING ELECTROPLATING LAYER ON NON-CONDUCTIVE MATERIAL SURFACE

(57)Abstract:

PURPOSE: To easily electroplate a non-conductive material with Cu by forming an Mn oxide layer on the material surface and dipping the material in a specified org. monomer soln. to form a conductive polymer coating film.

CONSTITUTION: The surface of a non-conductive material is dipped in a soln. of an alkaline permanganate and cleaned, and an Mn oxide layer is formed on the surface. The material is then dipped in an org. monomer soln. kept at pH <4 and contg. 1-9g/l of aniline or its derivative, at least one kind among borofluoric acid, perchloric acid, sulfuric acid, aromatic sulfonic acid or further at least one kind of the fine powder of the conductive material such as C, Pd-Sn colloid, copper sulfide, nickel sulfide and ITO. An org. monomer is converted into a polymer film by the oxidation reaction of the org. monomer with manganese oxide to make the non-conductive material conductive. Consequently, the non-conductive material surface is easily electroplated with Cu without using troublesome chemical plating.

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CLAIMS

[Claim(s)]

[Claim 1]A plating method of non-conducting material processing non-conducting material at the following process : (One) non-conducting material is processed with an alkaline permanganate solution, non-conducting material from a process and the (2) above-mentioned (1) process in which resemble the surface and a manganic acid ghost layer is made to form being immersed in an acidic solution of an organic monomer which can form a conductive polymer by oxidative polymerization, and, A process which makes a conductive polymer tunic form in the surface of non-conducting material by oxidation of a manganic acid ghost layer, a process which makes an electrolytic copper metal skin form in material from the (3) above-mentioned (2) process directly.

[Claim 2]In the plating method according to claim 1, an acidic solution of an organic monomer in (2) processes, A plating method which is pH four or less acidic solution which contains at least one sort of aniline, pyrrole, a thiophene, a franc, and its derivative in 1-9 g/l, and contains at least one sort of Howe fluoric acid, perchloric acid, sulfuric acid, and aromatic sulfonic acid.

[Claim 3]A plating method with which an acidic solution of an organic monomer in (2) processes contains at least one sort of impalpable powder of a conductive substance further chosen from carbon, palladium tin colloid, copper sulfide, a nickel sulfide, and ITO in the plating method according to claim 2.

[Claim 4]A printed wired board which carried out through hole plating method:(1) perforation of processing a double-sided printed wiring board or a multilayer printed wiring board at the following process of a printed wired board by which it is characterized, and was washed is processed with an alkaline permanganate solution, A printed wired board from a process and the (2) above-mentioned (1) process which makes a manganic acid ghost layer form in a non-conducting portion of a through hole wall is immersed in an acidic solution of an organic monomer which can form a conductive polymer by oxidative polymerization, A process which makes a conductive polymer tunic form in a non-conducting bill-of-materials side of a through hole wall by oxidation of a manganic acid ghost layer, a process which makes an electrolytic copper metal skin form in a non-conducting bill-of-materials side of a through hole wall of a printed wired board from the (3) above-mentioned (2) process directly.

[Claim 5]In the plating method according to claim 4, an acidic solution of an organic monomer in (2) processes, A plating method which is pH four or less acidic solution which contains at least one sort of aniline, pyrrole, a thiophene, a franc, and its derivative in 1-9 g/l, and contains at least one sort of Howe fluoric acid, perchloric acid, sulfuric acid, and aromatic sulfonic acid.

[Claim 6]A plating method with which an acidic solution of an organic monomer in (2) processes contains at least one sort of impalpable powder of a conductive substance further chosen from carbon, palladium tin colloid, copper sulfide, a nickel sulfide, and ITO in the plating method according to claim 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the method of making an electrolytic copper metal skin forming in the through hole of a printed wired board directly in more detail, about the method of making an electrolytic copper metal skin forming in a non-conducting material-list side directly.

[0002]That as used herein it is with "%" shall mean "weight %."

[0003]

[Description of the Prior Art]As a method of performing through hole plating to a printed wired board, the subtractive process is mainly adopted. In this method, after flow-izing an insulating part by the substrate which pasted up copper foil on the facing and the inner surface which consist of insulation bases depositing thin non-electrolytic copper plating in the insulating part inside a drilling opium poppy and a hole, a thick copper film is formed by electrolytic copper plating, the flow between copper foil is secured, and an electric circuit is created.

[0004]This method is a method that the reliability already established technically is high.

It has a track record which has continued being used for about 20 years.

However, this method makes indispensable the electroless deposition process of needing a complicated head end process, in order to attain flow-ization of an insulating part. it is necessary to use toxic high formalin as a reducing agent which the plating solution used at this electroless deposition process is [reducing agent] that in which autolysis nature is strongly, and needs [reducing agent] strict control of bath, and deposits copper -- further -- **** -- it has various faults, such as requiring a long time also for obtaining a thin copper film.

[0005]

[Problem(s) to be Solved by the Invention]Therefore, this invention, without needing the non-electrolytic copper plating process used as the big skill constraint in a conventional method, Flow-ization of an insulating part is enabled only according to an electrolytic copper plating process, and improvement in productivity is primarily aimed at by simplification of down stream processing, shortening of processing time, improvement of work environment, etc.

[0006]

[Means for Solving the Problem]this invention person found out that the above-mentioned purpose could be attained, when adopting combining a specific process, as a result of repeating research wholeheartedly in view of the actual condition of the above art. Combination of this specific process found out a useful thing, also when making an electrolytic copper metal skin form in a common non-conducting material directly.

[0007]That is, this invention provides a following method:

A plating method of non-conducting material processing non-conducting material at the following process : 1 (One) non-conducting material is processed with an alkaline permanganate solution, non-conducting material from a process and the (2) above-mentioned (1) process in which resemble the surface and a manganic acid ghost layer is made to form being immersed in an acidic solution of an organic monomer which can form a conductive polymer by oxidative polymerization, and, A process which makes a conductive polymer tunic form in the surface of non-conducting material by oxidation of a manganic acid ghost layer, a process which makes an electrolytic copper metal skin form in material from the (3) above-mentioned (2) process directly.

[0008]2 In a plating method given in the above-mentioned paragraph 1, an acidic solution of an organic monomer in (2) processes, A plating method which is pH four or less acidic solution which contains at least one sort of aniline, pyrrole, a thiophene, a franc, and its derivative in 1-9 g/l, and contains at least one sort of Howe fluoric acid, perchloric acid, sulfuric acid, and aromatic sulfonic acid.

[0009]3 A plating method with which an acidic solution of an organic monomer in (2) processes contains at least

one sort of impalpable powder of a conductive substance further chosen from carbon, palladium tin colloid, copper sulfide, a nickel sulfide, and ITO in a plating method given in the above-mentioned paragraph 2.

[0010]4 A printed wired board which carried out through hole plating method:(1) perforation of processing a double-sided printed wiring board or a multilayer printed wiring board at the following process of a printed wired board by which it is characterized, and was washed is processed with an alkaline permanganate solution, A printed wired board from a process and the (2) above-mentioned (1) process which makes a manganic acid ghost layer form in a non-conducting portion of a through hole wall is immersed in an acidic solution of an organic monomer which can form a conductive polymer by oxidative polymerization, A process which makes a conductive polymer tunic form in a non-conducting bill-of-materials side of a through hole wall by oxidation of a manganic acid ghost layer, a process which makes an electrolytic copper metal skin form in a non-conducting bill-of-materials side of a through hole wall of a printed wired board from the (3) above-mentioned (2) process directly.

[0011]5 In a plating method given in the above-mentioned paragraph 4, an acidic solution of an organic monomer in (2) processes, A plating method which is pH four or less acidic solution which contains at least one sort of aniline, pyrrole, a thiophene, a franc, and its derivative in 1-9 g/l, and contains at least one sort of Howe fluoric acid, perchloric acid, sulfuric acid, and aromatic sulfonic acid.

[0012]6 A plating method with which an acidic solution of an organic monomer in (2) processes contains at least one sort of impalpable powder of a conductive substance further chosen from carbon, palladium tin colloid, copper sulfide, a nickel sulfide, and ITO in a plating method given in the above-mentioned paragraph 5.

[0013]this invention method can make an electrolytic copper metal skin form in an insulating part of a through hole of a general non-conducting material-list side, a double-sided printed-circuit board, and a multilayer printed circuit board, etc. directly. However, below, it explains one by one for every process by making formation of a direct electrolytic copper metal skin to a through hole insulating part of a double-sided printed-circuit board or a multilayer printed circuit board into an example.

[0014]In a swelling this invention method, swelling processing of the printed-circuit board (henceforth a test specimen) perforated and washed is first carried out in accordance with a conventional method. Although not limited, especially the swelling processing conditions will be as follows if the example is given.

[0015]

glycol ether system solvent 50 - 900 ml/l -- more -- desirable -- 100 - 300 ml/l sodium hydroxide 1-50 g/l, more -- desirable -- 5-30-g/l surface-active agent Optimum dose treatment temperature 20-80 ** -- more -- desirable -- 40-70 ** processing time 1 - 10 minutes -- more -- desirable -- a part for 2 - 7 -- permanganate solution **** -- subsequently in accordance with a conventional method, an etching process by a permanganate solution is presented with a test specimen. Although etching process conditions are not limited in particular, either, it will be as follows if the example is given.

[0016]

KMnO₄ or 20-100 g/l of NaMnO₄, 40-60 g/l more preferably KOH or 5-50 g/l of NaOH(s), more -- desirable -- 30-40-g/l surface-active agent Optimum dose treatment temperature 50-95 ** -- more -- desirable -- 70-90 ** processing time 1 - by 2 - an 8-minute conventional method more preferably for 15 minutes. Although neutralization processing of the test specimen which swelling processing was carried out and received an etching process by a permanganate solution is carried out successively and a formed manganic acid ghost layer is removed, Since oxidative polymerization of an organic monomer is promoted after continuing organic monomer solution immersion using an operation as an oxidizer of a manganic acid ghost layer, it is made to remain as it is in this invention.

[0017]By the organic monomer solution immersion following **, a test specimen is immersed in an acidic solution of an organic monomer, as an organic monomer -- aniline, pyrrole, a thiophene, francs, and these derivatives (aniline sulfate.) o-aniline sulfonic acid, m-aminophenol, m-aminobenzoic acid, N-methylpyrrole, 3-methylthiophene, etc. -- etc. -- it is illustrated and these one sort or two sorts or more are used. As a solvent of a solution, alcohols, such as water, methanol, ethanol, n-propanol, and isopropanol, are mentioned, and these one sort or two sorts or more are used. Concentration of an organic monomer in this acidic solution shall be about 1-9 g/l. When monomer concentration is too high, a loss by decomposition of a monomer not only increases, but hydrolysis of a monomer is promoted and a life of liquid becomes short by accumulation of hydrolyzate generated so much. On the other hand, when monomer concentration is too low, generating of a conductive polymer becomes insufficient and the deposit nature of electrolytic copper plating falls. This acidic solution makes **** indispensable or less by pH four, including at least one sort of Howe fluoric acid, perchloric acid, sulfuric acid, and aromatic sulfonic acid. In such an acidic solution, since dissolution removal of the

manganic acid ghost layer slightly formed in a copper foil portion of a through hole of a test specimen in a previous process is carried out into a short time, a polymer layer is selectively formed only in a non-conducting portion in a through hole of a test specimen. Although thickness in particular of a polymer layer is not limited, it is preferred to be referred to as about 0.5–2 micrometers. Adjustment of thickness of a polymer layer can be performed by adjusting manganic acid ghost layer thickness and monomer concentration. Thus, since a formed polymer layer has advanced conductivity and moderate surface roughness, formation of an electrolytic copper plating layer excellent in adhesion of it is attained.

[0018]In order to improve the conductivity of a polymer layer, an acidic solution of an organic monomer can be made to contain at least one sort of impalpable powder of a conductive substance chosen from carbon, palladium tin colloid, copper sulfide, a nickel sulfide, and ITO in this invention. As for these conductive substances, in order to acquire good dispersibility, it is preferred to consider it as a particle size of about 0.1–1 micrometer, and to consider it as concentration of about 1–10 g/l. When using these conductive substances together, one sort of composite polymer layers which distributed a conductive substance are formed. Although conductivity falls and electrolytic copper plating may be unable to perform easily a polymer layer formed of oxidative polymerization good due to reduction at the time of electroplating, when it is a composite polymer layer, a conductive fall is controlled and more reliable through-hole plating is obtained.

[0019]activation **** -- subsequently, if necessary, activation will be presented with a test specimen in accordance with a conventional method. Although not limited, activation liquid and especially its condition will be as follows if the example is given.

sulfuric acid (98%) 10 – 150 ml/l -- more -- desirable -- 50 – 100 ml/l treatment temperature 10–30 **, more – – desirable -- 15–25 ** processing time 0.1 – 3 minutes -- more -- desirable -- 0.5 – when performing this activation for 1 minute, a copper foil portion of a through hole of a test specimen is activated more by fitness, and adhesion with an electroplating layer formed at a process of continuing is improved more.

[0020]electroplating **** -- subsequently in accordance with a conventional method, electrolytic copper plating treatment is presented with a test specimen. Although not limited, an electrolytic copper plating treatment bath and especially the processing condition will be as follows if the example is given.

[0021]Copper sulfate plating bath Copper sulfate It is 60–80–g/l sulfuric acid more preferably 40–100 g/l. 100–300 g/l, It is a 150–250–g/l chloride ion more preferably. 30 – 100 mg/l, It is a 40–80mg [l.] brightening agent more preferably. Optimum dose Treatment temperature 10–40 **, It is 15–30 ** more preferably. Cathode current density 0.5 – 10 A/dm², It is a 1 – 5 A/dm² pyrophoric acid plating bath more preferably. Copper pyrophosphate 50–100 g/l, It is 60–80–g/l potassium pyrophosphate more preferably. 200–500 g/l, It is a 250–400–g/l ammonia solution (28%) more preferably. 1 – 7 ml/l, It is a 2–4ml [l.] brightening agent more preferably. Optimum dose Treatment temperature 40–70 **, It is 50–60 ** more preferably. Cathode current density It is applicable also to formation of a direct electrolytic copper metal skin to a general 0.5 – 8 A/dm² and non-conducting material in which a 1 – 5 A/dm² this invention method does not have a copper foil coat more preferably.

[0022] [Effect of the Invention]According to this invention, an electrolytic copper metal skin can be directly formed in a non-conducting material-list side, without passing through a non-electrolytic copper plating process. Therefore, since time until it results in formation of an electrolytic copper metal skin is shortened by about about 1 / 3 as compared with the conventional method which makes a non-electrolytic copper plating process indispensable, industrial profits are very large.

[0023] [Example]An example is shown below and the place by which it is characterized [of this invention] is clarified further.

[0024]After processing FR-4 substrate which carried out example 1 hole dawn for 5 minutes at 60 ** among the alkaline solution (swelling liquid) containing a water soluble solvent and a surface-active agent, Etching washing of the copper foil portion is carried out for 1 minute at 25 ** among the solution (soft etching liquid) containing 200 g/l of sodium persulfate, and sulfuric acid 10 ml/l, It rinsed and processed for 8 minutes at 80 ** among the solution (permanganic acid etching reagent) which contains 50 g/l of potassium permanganate, and 20 g/l of sodium hydroxide further.

[0025]After fully rinsing the substrate processed as mentioned above, it was immersed in the solution containing 3 g/l of pyrrole, and perchloric acid 25 ml/l for 3 minutes at 20 **. Subsequently, the substrate was rinsed, after being activated for about 30 seconds with the activity liquid containing 50ml/l. of sulfuric acid, the following

copper sulfate plating bath was used and electroplating was performed for 5 minutes under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0026]

Copper sulfate 80-g/l sulfuric acid 180-g/l chloride ion Copper sulfate brightening agent for 50 mg/l printed wired boards 2.5 ml/l (a trademark "top RUCHINA 81-HL" and made in Okuno Pharmaceutical industry)

After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

[0027]After having carried out swelling processing of the FR-4 substrate which carried out example 2 hole dawn like Example 1, carrying out permanganic acid etching and fully rinsing, it was immersed for 3 minutes at 20 ** into the liquid containing 3 g/l of pyrrole, perchloric acid 25 ml/l, and 10 g/l of particle carbon (about 0.2 micrometer). Subsequently, the substrate was rinsed, after being activated for about 30 seconds with the activity liquid containing sulfuric acid 50 ml/l, the same copper sulfate plating bath as Example 1 was used, and electroplating was performed for 1 minute under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0028]After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

[0029]After having carried out swelling processing of the FR-4 substrate which carried out example 3 hole dawn like Example 1, carrying out permanganic acid etching and fully rinsing, it was immersed for 3 minutes at 20 ** into the liquid containing 5 g/l of pyrrole, Howe fluoric acid 5 ml/l, and 10 g/l of particle carbon (about 0.2 micrometer). Subsequently, the substrate was rinsed, after being activated for about 30 seconds with the activity liquid containing sulfuric acid 50 ml/l, the same copper sulfate plating bath as Example 1 was used, and electroplating was performed for 3 minutes under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0030]After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

[0031]After having carried out swelling processing of the six-layer multilayer substrate which perforated example 4 like Example 1, carrying out permanganic acid etching and fully rinsing, it was immersed for 5 minutes at 10 ** into the liquid containing 5 g/l of pyrrole, Para toluenesulfonic acid 25 ml/l, and 5 g/l of copper sulfide (about 1 micrometer). Subsequently, the substrate was rinsed, after being activated for about 30 seconds with the activity liquid containing sulfuric acid 50 ml/l, the same copper sulfate plating bath as Example 1 was used, and electroplating was performed for 1 minute under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0032]After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

[0033]Swelling processing of the FR-4 substrate which carried out example 5 hole dawn is carried out like Example 1, After carrying out permanganic acid etching and fully rinsing, it was immersed for 2 minutes at 20 ** into the liquid containing 8 g/l of pyrrole, 30 g/l of ethylene glycol, 50 g/l of sulfosalicylic acid, and 5 g/l of palladium tin colloid. Subsequently, the substrate was rinsed, after being activated for about 30 seconds with the activity liquid containing sulfuric acid 50 ml/l, the same copper sulfate plating bath as Example 1 was used, and electroplating was performed for 2 minutes under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0034]After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

[0035]After having carried out swelling processing of the FR-4 substrate which carried out example 6 hole dawn like Example 1, carrying out permanganic acid etching and fully rinsing, it was immersed for 3 minutes at 5 ** into the liquid containing 8 g/l of aniline sulfate, sulfuric acid 100 ml/l, and 10 g/l of carbon impalpable powder. Subsequently, after rinsing a substrate, the same copper sulfate plating bath as Example 1 was used, and electroplating was performed for 2 minutes under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0036]After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

[0037]After having carried out swelling processing of the FR-4 substrate which carried out example 7 hole dawn like Example 1, carrying out permanganic acid etching and fully rinsing, it was immersed for 3 minutes at 5 ** into the liquid containing 8 g/l of m-aminophenols, sulfuric acid 50 ml/l, and 3 g/l of ITO impalpable powder.

Subsequently, after rinsing a substrate, the same copper sulfate plating bath as Example 1 was used, and electroplating was performed for 2 minutes under the condition of the temperature of 25 **, and cathode-current-density 2.5 A/dm².

[0038]After the completion of plating, the through hole wall of the substrate was thoroughly covered with the copper plating film.

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(54)【発明の名称】 非導電性材料表面に電気メッキ層を直接形成する方法

(57)【要約】

【目的】 非導電性材料に導電性を付与するに際し、無電解銅メッキ工程を必要とすることなく、電気銅メッキ工程のみによって絶縁性部分の導通化を可能とし、処理工程の簡略化、処理時間の短縮、作業環境の改善などにより、生産性の向上を図ることを主な目的とする。

【構成】 非導電性材料を下記の工程で処理することを特徴とする非導電性材料のメッキ方法：

(1) 非導電性材料をアルカリ性過マンガン酸塩溶液により処理し、その表面にマンガン酸化物層を形成させる工程、(2) 上記(1)工程からの非導電性材料を酸化重合により導電性ポリマーを形成し得る有機モノマーの酸性溶液に浸漬して、マンガン酸化物層の酸化作用により非導電性材料の表面に導電性ポリマー被膜を形成させる工程、(3) 上記(2)工程からの材料に電気銅メッキ層を直接形成させる工程。

【特許請求の範囲】

【請求項1】非導電性材料を下記の工程で処理することを特徴とする非導電性材料のメッキ方法：

(1) 非導電性材料をアルカリ性過マンガン酸塩溶液により処理し、その表面にマンガン酸化物層を形成させる工程、(2) 上記(1)工程からの非導電性材料を酸化重合により導電性ポリマーを形成し得る有機モノマーの酸性溶液に浸漬して、マンガン酸化物層の酸化作用により非導電性材料の表面に導電性ポリマー被膜を形成させる工程、(3) 上記(2)工程からの材料に電気銅メッキ層を直接形成させる工程。

【請求項2】請求項1に記載のメッキ方法において、(2)工程における有機モノマーの酸性溶液が、アニリン、ビロール、チオフェン、フランおよびその誘導体の少なくとも1種を1～9g／1の範囲で含み、且つホウフッ酸、過塩素酸、硫酸および芳香族スルホン酸の少なくとも1種を含むpH4以下の酸性溶液であるメッキ方法。

【請求項3】請求項2に記載のメッキ方法において、(2)工程における有機モノマーの酸性溶液が、さらにカーボン、バラジウムースズコロイド、硫化銅、硫化ニッケルおよびITOから選ばれた導電性物質の少なくとも1種の微粉末を含有するメッキ方法。

【請求項4】両面プリント配線板或いは多層プリント配線板を下記の工程で処理することを特徴とするプリント配線板のスルーホールメッキ方法：

(1) 穴開けして洗浄したプリント配線板をアルカリ性過マンガン酸塩溶液により処理し、スルーホール内壁の非導電性部分にマンガン酸化物層を形成させる工程、

(2) 上記(1)工程からのプリント配線板を酸化重合により導電性ポリマーを形成し得る有機モノマーの酸性溶液に浸漬して、マンガン酸化物層の酸化作用によりスルーホール内壁の非導電性部分表面に導電性ポリマー被膜を形成させる工程、(3) 上記(2)工程からのプリント配線板のスルーホール内壁の非導電性部分表面に電気銅メッキ層を直接形成させる工程。

【請求項5】請求項4に記載のメッキ方法において、(2)工程における有機モノマーの酸性溶液が、アニリン、ビロール、チオフェン、フランおよびその誘導体の少なくとも1種を1～9g／1の範囲で含み、且つホウフッ酸、過塩素酸、硫酸および芳香族スルホン酸の少なくとも1種を含むpH4以下の酸性溶液であるメッキ方法。

【請求項6】請求項5に記載のメッキ方法において、(2)工程における有機モノマーの酸性溶液が、さらにカーボン、バラジウムースズコロイド、硫化銅、硫化ニッケルおよびITOから選ばれた導電性物質の少なくとも1種の微粉末を含有するメッキ方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、非導電性材料表面に直接電気銅メッキ層を形成させる方法に関し、さらに詳しくはプリント配線板のスルーホールに直接電気銅メッキ層を形成させる方法に関する。

【0002】本明細書において、"%"とあるのは、"重量%"を意味するものとする。

【0003】

【従来技術とその問題点】プリント配線板に対してスルーホールメッキを行なう方法としては、主としてサブトラクティブ法が採用されている。この方法では、絶縁性基材からなる表面材および内面に銅箔を接着した基板を穴明けし、穴内部の絶縁性部分に薄い無電解銅メッキを析出させることにより絶縁性部分を導通化した後、電気銅メッキにより厚い銅皮膜を形成して、銅箔間の導通を確保し、電気回路を作成する。

【0004】この方法は、すでに技術的に確立された信頼性の高い方法であり、約20年使用され続けてきた実績を有している。しかしながら、この方法は、絶縁性部分の導通化を図るために、複雑な前処理工程を必要とする無電解メッキ工程を必須とする。この無電解メッキ工程で使用するメッキ液は、自己分解性が強いため、厳密な浴管理を必要とし、また銅を析出させる還元剤として毒性の高いホルマリンを使用する必要があり、さらに極く薄い銅皮膜を得るにも長時間を要するなどの種々の欠点を有している。

【0005】

【発明が解決しようとする課題】従って、本発明は、従来法における大きな技術的制約となっていた無電解銅メッキ工程を必要とすることなく、電気銅メッキ工程のみによって絶縁性部分の導通化を可能とし、処理工程の簡略化、処理時間の短縮、作業環境の改善などにより、生産性の向上を図ることを主な目的とする。

【0006】

【課題を解決するための手段】本発明者は、上記の様な技術の現状に鑑みて鋭意研究を重ねた結果、特定の工程を組合せて採用する場合には、上記の目的を達成し得ることを見出した。また、この特定工程の組合せは、一般の非導電性材料に直接電気銅メッキ層を形成させる場合にも、有用であることを見出した。

【0007】即ち、本発明は、下記の方法を提供するものである：

1 非導電性材料を下記の工程で処理することを特徴とする非導電性材料のメッキ方法：

(1) 非導電性材料をアルカリ性過マンガン酸塩溶液により処理し、その表面にマンガン酸化物層を形成させる工程、(2) 上記(1)工程からの非導電性材料を酸化重合により導電性ポリマーを形成し得る有機モノマーの酸性溶液に浸漬して、マンガン酸化物層の酸化作用により非導電性材料の表面に導電性ポリマー被膜を形成させる工程、(3) 上記(2)工程からの材料に電気銅メ

ッキ層を直接形成させる工程。

【0008】2 上記項1に記載のメッキ方法において、(2)工程における有機モノマーの酸性溶液が、アニリン、ビロール、チオフェン、フランおよびその誘導体の少なくとも1種を1~9g/1の範囲で含み、且つホウフッ酸、過塩素酸、硫酸および芳香族スルホン酸の少なくとも1種を含むpH4以下の酸性溶液であるメッキ方法。

【0009】3 上記項2に記載のメッキ方法において、(2)工程における有機モノマーの酸性溶液が、さらにカーボン、バラジウムースズコロイド、硫化銅、硫化ニッケルおよびITOから選ばれた導電性物質の少なくとも1種の微粉末を含有するメッキ方法。

【0010】4 両面プリント配線板或いは多層プリント配線板を下記の工程で処理することを特徴とするプリント配線板のスルーホールメッキ方法：

(1) 穴開けして洗浄したプリント配線板をアルカリ性過マンガン酸塩溶液により処理し、スルーホール内壁の非導電性部分にマンガン酸化物層を形成させる工程、

(2) 上記(1)工程からのプリント配線板を酸化重合により導電性ポリマーを形成し得る有機モノマーの酸性溶液に浸漬して、マンガン酸化物層の酸化作用によりスルーホール内壁の非導電性部分表面に導電性ポリマー被膜を形成させる工程、(3) 上記(2)工程からのプリント配線板のスルーホール内壁の非導電性部分表面に電気銅メッキ層を直接形成させる工程。

方、モノマー濃度が低すぎる場合には、導電性ポリマーの生成が不十分となり、電気銅めっきの析出性が低下する。さらに、この酸性溶液は、ホウツ酸、過塩素酸、硫酸および芳香族スルホン酸の少なくとも1種を含み且つpH4以下であるを必須とする。この様な酸性溶液中では、前工程において供試材のスルーホールの銅箔部分に僅かに形成されたマンガン酸化物層が、短時間内に溶解除去されるので、供試材のスルーホール内の非導電性部分にのみ選択的にポリマー層が形成される。ポリマー層の厚さは、特に限定されるものではないが、0.5～2μm程度とすることが好ましい。ポリマー層の厚さの調整は、マンガン酸化物層の厚さとモノマー濃度を調整することにより、行なうことができる。この様にして形成されたポリマー層は、高度の導電性と適度の表面粗度とを有しているので、密着性に優れた電気銅めっき層の形成が可能となる。

【0018】本発明においては、ポリマー層の導電性を改善するために、カーボン、パラジウムースズコロイ*

硫酸(98%)	10～150ml/l、より好ましくは50～100ml/l
処理温度	10～30°C、より好ましくは15～25°C
処理時間	0.1～3分、より好ましくは0.5～1分

この活性化処理を行なう場合には、供試材のスルーホールの銅箔部分がより良好に活性化され、引続く工程で形成される電気めっき層との密着性がより高められる。

【0020】電気メッキ処理

次いで、供試材を常法に従って電気銅メッキ処理に供す*

硫酸銅メッキ浴	
硫酸銅	40～100g/l、より好ましくは60～80g/l
硫酸	100～300g/l、より好ましくは150～250g/l
塩素イオン	30～100mg/l、より好ましくは40～80mg/l
光沢剤	適量
処理温度	10～40°C、より好ましくは15～30°C
陰極電流密度	0.5～10A/dm ² 、より好ましくは1～5A/dm ²
ビロリン酸銅メッキ浴	
ビロリン酸銅	50～100g/l、より好ましくは60～80g/l
ビロリン酸カリウム	200～500g/l、より好ましくは250～400g/l
アンモニア水(28%)	1～7ml/l、より好ましくは2～4ml/l
光沢剤	適量
処理温度	40～70°C、より好ましくは50～60°C
陰極電流密度	0.5～8A/dm ² 、より好ましくは1～5A/dm ²

本発明方法は、銅箔層を有しない一般的な非導電性材料への直接電気銅メッキ層の形成にも、適用できる。

【0022】

【発明の効果】本発明によれば、無電解銅メッキ工程を経ることなく、非導電性材料表面に直接電気銅メッキ層を形成することができる。従って、電気銅メッキ層の形成に至るまでの時間が、無電解銅メッキ工程を必須とする従来法に比して、約1/3程度に短縮されるので、産業上の利益は、極めて大きい。

【0023】

*ド、硫化銅、硫化ニッケルおよびITOから選ばれた導電性物質の少なくとも1種の微粉末を有機モノマーの酸性溶液に含有させておくことが出来る。これらの導電性物質は、良好な分散性を得るために、0.1～1μm程度の粒度とし、かつ濃度1～10g/l程度とすることが好ましい。これらの導電性物質を併用する場合には、導電性物質を分散した1種のコンポジットポリマー層が形成される。酸化重合により形成されたポリマー層は、電気めっき時の還元により、導電性が低下して電気銅めっきが良好に行ない難い場合があるが、コンポジットポリマー層の場合には、導電性の低下が抑制され、より信頼性の高いスルーホールめっきが得られる。

【0019】活性化処理

次いで、必要ならば、供試材を常法に従って活性化処理に供する。活性化処理液およびその条件は、特に限定されるものではないが、その具体例を挙げれば、下記の通りである。

【0020】

※る。電気銅メッキ処理浴および処理条件は、特に限定されるものではないが、その具体例を挙げれば、下記の通りである。

【0021】

【実施例】以下に実施例を示し、本発明の特徴とすることをより一層明確にする。

【0024】実施例1

穴明けしたFR-4基板を水溶性溶剤と界面活性剤を含むアルカリ性溶液(膨潤液)中60°Cで5分間処理した後、過硫酸ナトリウム200g/lと硫酸10ml/lとを含む水溶液(ソフトエッティング液)中25°Cで1分間銅箔部分をエッティング洗浄し、水洗し、さらに過マンガン酸カリウム50g/lと水酸化ナトリウム20g/50mlとを含む水溶液(過マンガン酸エッティング液)中80

°Cで8分間処理した。

【0025】上記の様にして処理した基板を十分に水洗した後、ピロール3g/1と過塩素酸25m1/1とを含む水溶液に20°Cで3分間浸漬した。次いで、基板を水洗し、硫酸50m1/1を含む活性液により約30秒間活性化した後、下記の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に5分間電気メッキを行なった。

【0026】

硫酸銅	80g/1	10
硫酸	180g/1	
塩素イオン	50mg/1	
プリント配線板用		
硫酸銅光沢剤	2.5m1/1	

(商標“トップルチナ81-HL”、奥野製薬工業(株)製)

メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。

【0027】実施例2

穴明けしたFR-4基板を実施例1と同様にして膨潤処理し、過マンガン酸エッティングし、十分に水洗した後、ピロール3g/1、過塩素酸25m1/1および微粒子カーボン(約0.2μm)10g/1を含む液中に20°Cで3分間浸漬した。次いで、基板を水洗し、硫酸50m1/1を含む活性液により約30秒間活性化した後、実施例1と同様の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に1分間電気メッキを行なった。

【0028】メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。

【0029】実施例3

穴明けしたFR-4基板を実施例1と同様にして膨潤処理し、過マンガン酸エッティングし、十分に水洗した後、ピロール5g/1、ホウツ酸5m1/1および微粒子カーボン(約0.2μm)10g/1を含む液中に20°Cで3分間浸漬した。次いで、基板を水洗し、硫酸50m1/1を含む活性液により約30秒間活性化した後、実施例1と同様の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に3分間電気メッキを行なった。

【0030】メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。

【0031】実施例4

穴開けした6層多層基板を実施例1と同様にして膨潤処

理し、過マンガン酸エッティングし、十分に水洗した後、ピロール5g/1、バラトルエンスルホン酸25m1/1および硫化銅(約1μm)5g/1を含む液中に10°Cで5分間浸漬した。次いで、基板を水洗し、硫酸50m1/1を含む活性液により約30秒間活性化した後、実施例1と同様の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に1分間電気メッキを行なった。

【0032】メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。

【0033】実施例5

穴明けしたFR-4基板を実施例1と同様にして膨潤処理し、過マンガン酸エッティングし、十分に水洗した後、ピロール8g/1、エチレングリコール30g/1、スルホサリチル酸50g/1およびバラジウムースズクロイド5g/1を含む液中に20°Cで2分間浸漬した。次いで、基板を水洗し、硫酸50m1/1を含む活性液により約30秒間活性化した後、実施例1と同様の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に2分間電気メッキを行なった。

【0034】メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。

【0035】実施例6

穴明けしたFR-4基板を実施例1と同様にして膨潤処理し、過マンガン酸エッティングし、十分に水洗した後、硫酸アニリン8g/1、硫酸100m1/1およびカーボン微粉末10g/1を含む液中に5°Cで3分間浸漬した。次いで、基板を水洗した後、実施例1と同様の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に2分間電気メッキを行なった。

【0036】メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。

【0037】実施例7

穴明けしたFR-4基板を実施例1と同様にして膨潤処理し、過マンガン酸エッティングし、十分に水洗した後、m-アミノフェノール8g/1、硫酸50m1/1およびITO微粉末3g/1を含む液中に5°Cで3分間浸漬した。次いで、基板を水洗した後、実施例1と同様の硫酸銅メッキ浴を使用して、温度25°C、陰極電流密度2.5A/dm²の条件下に2分間電気メッキを行なった。

【0038】メッキ完了後に、基板のスルーホール内壁は、完全に銅メッキ皮膜で覆われていた。